



### DECLARATION

I, Xie Shao, declare and state as follows:

1. I am one of the inventors named on the above-referenced patent application. I am currently a Division Manager in the Research and Development Division with Brewer Science Inc., and have been employed by Brewer Science Inc. for 10 years. I previously served as a Product Manager in the Chemical Division at Brewer Science Inc., and as Group Manager for the Anti-Reflective Coating Section of the Research and Development Group at Brewer Science Inc.

2. Under my direction and control, U.S. Patent No. 5,602,198 to Das et al. and U.S. Patent No. 6,010,956 to Takiguchi et al. were tested to show that the compositions disclosed by these references do not inherently possess the properties recited by the claims of this application.

#### U.S. PATENT NO. 5,602,198 TO DAS ET AL.

3. An acrylic resin solution was prepared exactly as described in Example 1 (beginning in column 5, line 55) except that the quantities of the various ingredients were scaled down. However, the same relative weight percentages were used. The exact amounts of the various compounds that were utilized are set forth in Table A.

Table A

	INGREDIENTS	WEIGHT (g)
Initial Charge	Xylene	19.98
Feed A	Cyclohexyl methacrylate	57.70
	2-hydroxybutyl acrylate	8.90
Feed B	2,2'-azobis(2-methylbutanenitrile) (AIBN)	3.33
	Xylene	19.98

After the polymer solution was prepared, it was used to prepare a film-forming composition exactly following the procedure described in Example I beginning in column 6, line 55 of the Das et al. patent, with the exceptions described herein. The procedure actually carried out was a scaled-down version, but the same parts by weight shown in the table at the bottom of column 6 in Das et al. were maintained. One of ordinary skill in the art would expect that scaling down the composition would not alter its performance, and that scaled-down, film-forming compositions would perform similarly to those made on a larger scale according to Example I of Das et al. The only other change to the procedure described in Example I was that ethanol was used in place of n-butanol. This should not alter the performance of the film-forming composition, as ethanol is one of the allowable monohydric alcohols set forth starting in column 3, line 39 of Das et al. The amount of each ingredient used is set forth in Table B.

Table B

INGREDIENTS	WEIGHT (g)
Polymer solution prepared above	13.335
CYMEL <sup>®</sup> 303	1.435
Xylene	0.73
n-Butyl acetate	0.73
Ethanol	0.365
TINUVIN 328	0.765
TINUVIN 292	0.095
K-CURE 1040 <sup>1</sup>	0.12

<sup>1</sup>K-Cure 1040 was used in place of Cypat-4040, which was used by Das et al. Both are 40% by weight solutions of p-toluenesulfonic acid.

The resulting formulation was coated onto silicon wafers according to the Prebake Thermal Stability Test and Film Shrinkage Test procedures outlined in the present patent application under the Detailed Description of the Preferred Embodiments section. The results of the Prebake Thermal Stability Test are set forth in Table C.

Table C

Prebake Thermal Stability Test					
Sample	30 s Prebake Temp	Thickness, Å	Post Bake Temp	Final Thickness, Å	% Removed
Das et al.	150°C	8889±590	100°C	8609±693	3.15

The Das et al. composition does not possess the property of being at least about 70% removed from the substrate following a Prebake Thermal Stability Test.

The results of the Film Shrinkage Test are set forth in Table D.

Table D

Film Shrinkage Test					
Sample	30 s Prebake Temp	Thickness, Å	Post Bake Temp	Final Thickness, Å	% Removed
Das et al.	150°C	8886±734	190°C	8364±570	5.87

The Das et al. composition does display the property of having less than about 15% film shrinkage when subjected to the Film Shrinkage Test.

U.S. PATENT NO. 6,010,956 TO TAKIGUCHI ET AL.

4. The following composition was prepared according to the methods described by Takiguchi et al. in Example 1, starting at column 13, line 65. The amounts of all ingredients were scaled-down from the described procedure, maintaining the same relative parts by weight. One of ordinary skill in the art would expect that a composition including the same ingredients on a smaller scale would perform in the same way as a composition prepared on a larger scale. EPON 829 or EPON 825 (Resolution Performance Products), a bisphenol A type epoxy resin, was used as a binder resin in place of N-673, an o-cresol novolak epoxy resin. While EPON 829 is not specifically listed in the example, it is a bisphenol A type epoxy resin, which is listed in the list of examples of binder resin at column 4, line 10, and is similar to Epikote 828 used in Example 2. The amounts of ingredients used are shown below in Table E.

Table E

INGREDIENT	WEIGHT (g)
EPON 829	25
Dicyandiamide	1.75
2-methyl imidazole amine	1.5
SWAZOL 1500	2.5
Diglycol Acetate	7.5
KS-66	0.5
LIONOL GREEN	0.625
MICROACE	2.5
AEROSIL	0.5
Barium Sulfate	15

The mixture was not mixed using a triple-roll mill as stated in the Takiguchi et al. example. The resulting material was spin-coated onto silicon wafers, but large particles remained in the composition. Sample 27-2 was ground with a mortar and pestle to remove large particles. The solid ingredients of Sample 28-1 were ground into a powder before the liquid components were added. Neither of these methods was successful in decreasing particle size significantly, so the material was used as is. In Sample 28-2A, EPON 829 was replaced with EPON 825.

The resulting formulation was coated onto silicon wafers according to the Prebake Thermal Stability and Film Shrinkage Test procedures described above. Film thickness measurements were made using the highest and lowest points on the Alpha Step. The results of the Prebake Thermal Stability Test are set forth below in Table F.

Table F

Prebake Thermal Stability Test					
Sample	30 s Prebake Temp	Thickness, $\mu\text{m}$	Post Bake Temp	Final Thickness, $\mu\text{m}$	% Removed
27-2	219°C	35 to 45	100°C	20 to 43	18.18
28-1	219°C	8.95	100°C	21	-134.00

As shown above, neither of the samples prepared according to Takiguchi et al. displayed the property of being at least about 70% removed from the substrate after the Prebake Thermal Stability Test.

The results of the Film Shrinkage Test are shown below in Table G.

Table G

Film Shrinkage Test					
Sample	30s Prebake Temp	Thickness, $\mu\text{m}$	Post Bake Temp	Final Thickness, $\mu\text{m}$	% Shrinkage
28-2A	190°C	10 to 21	240°C	28 to 45	-135.48
27-2	226°C	9.231 $\pm$ 0.952	226°C	9.309 $\pm$ 0.747	-0.84
27-2	219°C	9.227 $\pm$ 0.730	230°C	9.343 $\pm$ 0.577	-1.26

As seen from the results in the table, the sample exhibited very little sample shrinkage, but actually increased in size.

5. An additional composition according to Example 1 of the Takiguchi et al. patent was prepared in the same manner described above, except ECN 1299 was used as the polymer. As before, the amounts of the ingredients were scaled down, with the original percentage by weight of each ingredient being maintained. One of ordinary skill in the art would expect that a composition made on a smaller scale would perform similarly to the same composition made on a large scale.

ECN 1299 (poly[(o-cresyl glycidyl ether)-co-formaldehyde]) is an o-cresol novolak resin similar to the N-673 used in Example 1. The Takiguchi et al. patent lists o-cresol novolak resins as an example of suitable binder resins (column 4, line 2). The amounts of ingredients used in the composition are set forth in Table H.

Table H

INGREDIENT	WEIGHT (g)
ECN 1299	25
Dicyandiamide	1.75
2-methyl imidazole amine	1.5
SWAZOL 1500	2.5
Diglycol Acetate	7.5
KS-66	0.5
LIONOL GREEN	0.625
MICROACE	2.5
AEROSIL	0.5
Barium Sulfate	15

With this formulation, spin-coating of the sample onto silicon wafers would not yield a uniform film. As a result, some of the samples were diluted at a 2:1 ratio with the solvent used in this composition, and spin-coated onto silicon wafers according to the Prebake Thermal Stability Test procedure. The undiluted samples were also spin-coated onto a silicon wafer at 2,500 rpm in an attempt to achieve a more uniform layer. The film thickness of each layer was measured using the highest and lowest points on an Alpha Step. The results of the Prebake Thermal Stability Test are shown below in Table I.

Table I

Prebake Thermal Stability Test					
Sample	30s Prebake Temp	Thickness, $\mu\text{m}$	Post Bake Temp	Final Thickness, $\mu\text{m}$	% Shrinkage
35-2 <sup>1</sup>	219°C	0.59 to 4.02	100°C	0.65 to 4.82	-18.66
35-2 <sup>1</sup>	168°C	1.02 to 14.9	100°C	0.17 to 7.9	49.31
35-2 <sup>1</sup>	190°C	0.025 to 2.7	100°C	0.305 to 2.8	-13.94

<sup>1</sup> sample diluted at a 2:1 ratio

As shown above, despite changing the prebake and postbake temperatures, the composition according to Takiguchi et al. does not possess the property of being at least about 85% removed after the Prebake Thermal Stability Test.

The results of the Film Shrinkage Test are shown below in Table J.

Table J

Film Shrinkage Test					
Sample	30s Prebake Temp	Thickness, $\mu\text{m}$	Post Bake Temp	Final Thickness, $\mu\text{m}$	% Shrinkage
35-2 <sup>1</sup>	219°C	16.005	219°C	16.133	-0.80
35-2 <sup>2</sup>	219°C	39.9782	219°C	39.9917	-0.03
35-2 <sup>2</sup>	219°C	41 to 82	219°C	41 to 82	0.00
35-2 <sup>1</sup>	168°C	24.5	168°C	39.2	-7.35
35-2 <sup>1</sup>	190°C	0.52 to 9.8	190°C	9.8	0.00

<sup>1</sup> sample diluted 2:1

<sup>2</sup> undiluted sample, spun at 2,500 rpm

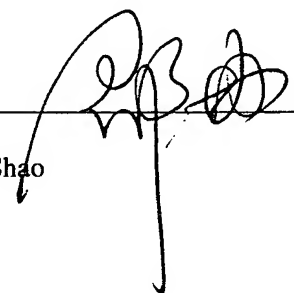
As shown in the table above, the composition according to the Takiguchi et al. patent does



possess the property of having less than about 15% shrinkage when subjected to the Film Shrinkage Test.

I further declare that all statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful, false statements and the like are punishable by fine or imprisonment, or both under § 1001 of Title 18 of the United States Code, and such willful, false statements may jeopardize the validity of any patents issued from the patent application.

Date: July 5, 2004

  
Xie Shao



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of:

LAMB, JAMES E. III et al.

Serial No.: 09/918,110

Filed: July 30, 2001

IMPROVED FILL MATERIAL FOR DUAL  
DAMASCENE PROCESSES

Docket No.: 27269-CON2

Group Art Unit No.: 1713

Examiner: K. Egwim

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Assistant Commissioner of Patents  
Washington, D.C. 20231

Sir:

DECLARATION

I, Xie Shao, declare and state as follows:

1. I am one of the inventors named on the above-referenced patent application. I am currently a Product Manager in the Chemical Division with Brewer Science, Inc., and have been employed by Brewer Science, Inc. for almost 8 years. I previously served as the Group Manager for the Anti-Reflective Coating Section of the Research and Development Group at Brewer Science, Inc.

2. Under my direction and control, the prior art references cited by the examiner in the February 8, 2000 office action of Application No. 09/383,785, and in the January 30, 2001 office action of Application No. 09/632,823, were tested to show that the compositions disclosed by those references do not inherently possess the properties recited by the claims of this application.

## U.S. PATENT NO. 5,602,198 TO DAS ET AL.

3. A polymer solution was prepared exactly as described in Example 1 (beginning in column 5, line 55) except that the quantities of the various ingredients were scaled down. However, the same relative weight percentages were used. The exact amounts of the various compounds that were utilized are set forth in Table A.

Table A

	INGREDIENTS	WEIGHT (g)
Initial Charge	Xylene	27.27
Feed A	Cyclohexyl methacrylate	78.75
	2-hydroxybutyl acrylate	12.12
Feed B	2-2'-azobis (2-methylbutanenitrile) (AIBN)	4.545
	Xylene	27.27

After cooling, the resultant mixture had a total solids content of about 63.6%.

After the polymer solution was prepared, it was then used to prepare a film-forming composition following the procedure described in Example I beginning in column 6, line 55 of the Das et al. patent. The only difference between the procedure actually carried out in the teachings of Das et al. is that the overall film forming composition was scaled down, but the same parts by weight shown in the table at the bottom of column 6 in the Das et al. patent were maintained. One skilled in the art would expect that scaling down the composition would not change its performance. That is, the scaled-down film forming composition should perform similarly to the larger scale, film-

forming composition set forth in Example I of Das et al. In this procedure, the amount of each ingredient utilized is set forth in Table B.

Table B

INGREDIENTS	WEIGHT (g)
Polymer solution prepared above	75.89
Cymel® 303	8.16
Xylene	4.15
Butyl acetate	4.16
Butanol	2.08
Tinuvin® 328	4.35
Tinuvin® 292	0.45
Cycat-4040	0.68

An attempt was made to spin-coat the resulting composition onto a 4-inch silicon wafer, however, the composition did not coat the wafer at all. That is, spin-coating resulted in a "lump" or "blob" of the composition in the middle of the wafer, with "strings" of the composition hanging from the blob or lump and extending towards the edges of the wafer. Thus, the instruments (neither the ellipsometer or the alpha stepper) were unable to give a consistent thickness measurement for purposes of carrying out the film shrinkage and pre-bake thermal stability tests. This composition could not be used as an anti-reflective coating composition or fill composition as it is not capable of coating substrate in an even remotely uniform manner.

## U.S. PATENT NO. 5,859,136 TO SCOPAZZI ET AL.

## A. Preparation of a Stabilizer Polymer Solution

A stabilizer polymer solution was prepared as described in column 10, lines 30-53 of the Scopazzi et al. patent except that the quantities of the various ingredients were scaled down. However, the same relative weight percentages were used. Table C sets forth the weights used in this procedure as compared to the weights disclosed by Scopazzi et al.

Table C

INGREDIENTS	SCOPAZZI ET AL. WEIGHTS (g)	SCALED DOWN WEIGHTS UTILIZED BY APPLICANTS (g)
Xylene	893.6	76.66
Styrene	477.3	40.94
Butyl methacrylate	492.6	42.26
Butyl acrylate	483.9	41.47
Hydroxy ethyl acrylate	263.9	22.64
Methacrylic acid	49.0	4.21
Isobornyl methacrylate	327.2	28.06
Tertiary butyl per acetate	127.1	10.91
Xylene	336.5	28.26
Beta catechol in isopropanol (10%)	0.9	0.00772
Glycidyl methacrylate	37.2	3.19
<i>n,n</i> -dimethyl amino propanol	0.5	0.0431
Xylene	8.5	0.729

## B. Preparation of Acrylic Polymer Dispersion 1

The procedure described in column 10, lines 55 et seq. was carried out as described through the point of that procedure which ends in column 11, line 5. Again, the quantities of ingredients used were scaled down as indicated in Table D.

Table D

INGREDIENTS	SCOPAZZI ET AL. WEIGHTS (g)	SCALED DOWN WEIGHTS UTILIZED BY APPLICANTS (g)
Stabilizer polymer solution	838.9	63.66
Ethyl acetate	28	2.14
Mineral spirits	231.0	17.51
Heptane	495.0	37.57
Isopropanol	100	7.60
<i>t</i> -butyl peroctoate	2.1	0.170
Heptane	25.0	1.90
Styrene	211.3	16.04
Hydroxy ethyl acrylate	281.4	21.32
Methyl methacrylate	522.0	39.61
Glycidyl methacrylate	130.8	9.94
Methacrylic acid	6.7	0.513
Methyl acrylate	193.6	14.71
Ethyl acetate	63.5	4.82
Heptane	126.0	9.58
Mineral Spirits	129.0	9.78

INGREDIENTS	SCOPAZZI ET AL. WEIGHTS (g)	SCALED DOWN WEIGHTS UTILIZED BY APPLICANTS (g)
<i>t</i> -butyl peroctoate	21.2	1.61
Stabilizer polymer solution	421.1	31.97

After the last stabilizer polymer solution addition step described in column 11, line 4 of Example 1, the reaction mixture formed a gel which could not be prepared into a coating composition. Thus, not only did this composition fail to form an anti-reflective coating film having the recited properties, it was incapable of being formed into any useable film at all due to the gel formation.

#### U.S. PATENT NO. 4,451,597 TO VICTORIUS

Example 2 of the Victorius patent was carried exactly as described to prepare the aluminum flake mill base described from column 13, line 43 through column 14, line 34 of that patent except that the ingredients were scaled down. Specifically, the ingredients were scaled down so that the total batch weight was 350 g, with the same relative percentages by weight being used as those described in Example 2 of the Victorius patent.

Attempts were made to subject the resulting composition to the pre-bake thermal stability test and film shrinkage test as described in the specification of the present application. However, it was not possible to subject the composition to the pre-bake thermal stability test as the composition formed a very rough, uneven film on the substrate surface which prevented the

equipment (ellipsometer and alpha stepper) from taking measurements of the film thickness. The poor quality of this film would make it entirely unsuitable for an anti-reflective coating or a fill composition.

With respect to the film shrinkage test, the composition performed quite poorly. The film shrinkage test was carried out utilizing ethyl lactate and following the procedure described in the present application. Due to the fact that the film was rough and uneven, the only thickness measurement taken was at the center point of the substrate, with the difference in the thickness at the center point being deemed the thickness lost which was used to calculate the percent shrinkage. Three different bake temperatures were tested, with five samples being subjected to each bake temperature (for a total of 15 samples). This data is set forth in Table E.

Table E

BAKE TEMPERATURE	PERCENT FILM SHRINKAGE OF 5 INDIVIDUAL SAMPLES				
160°C/60 sec bake	24.44%	23.83%	31.96%	22.06%	22.04%
150°C/60 sec bake followed by 205°C/60 sec bake	26.76%	43.40%	19.68%	25.98%	33.85%
205°C/60 sec bake	28.85%	38.46%	26.56%	26.91%	38.89%

Clearly, the films formed with the Victorious composition shrunk much more than the less than about 15% recited in the claims. This is further confirmed by absorbance measurements taken both before and after being subjected to the film shrinkage test. The samples exhibited dramatic



decreases in absorbance after the film shrinkage test, indicating that a large portion of the film had been removed by the solvent. This is shown in Table F.

Table F

BAKE TEMPERATURE	WAVELENGTH	DIFFERENCE IN ABSORBANCE BEFORE AND AFTER FILM SHRINKAGE TESTS	
		before stripping	after stripping
160°C/60 sec bake	193 nm	3.4087	0.9766
	248 nm	0.4686	0.0323
	365 nm	0.4140	0.0227
150°C/60 sec bake followed by 205°C/60 sec bake	193 nm	4.2572	1.0922
	248 nm	0.4196	0.0340
	365 nm	0.3653	0.0258
205°C/60 sec bake	193 nm	3.4133	1.1275
	248 nm	0.3897	0.0385
	365 nm	0.3428	0.0267

Similar results were obtained when determining the optical density (see Table G), further confirming that the film was substantially removed by the solvent.

Table G

BAKE TEMPERATURE	WAVELENGTH	DIFFERENCE IN OPTICAL DENSITY (1/μm) BEFORE AND AFTER FILM SHRINKAGE TESTS	
		before stripping	after stripping
160°C/60 sec bake	193 nm	29.6856	8.5048

BAKE TEMPERATURE	WAVELENGTH	DIFFERENCE IN OPTICAL DENSITY (1/ $\mu$ m) BEFORE AND AFTER FILM SHRINKAGE TESTS	
	248 nm	4.0806	0.2815
	365 nm	3.6051	0.1977
150°C/60 sec bake followed by 205°C/60 sec bake	193 nm	32.2151	9.0348
	248 nm	3.4705	0.2925
	365 nm	3.0221	0.2220
205°C/60 sec bake	193 nm	28.4251	9.3899
	248 nm	3.2457	0.3210
	365 nm	2.8544	0.2221

## U.S. PATENT NO. 4,727,100 TO VASTA

The procedure described in Example 1 of the Vasta patent was duplicated up to the point of the coating composition preparation (i.e., beginning at column 6, line 67 and ending at column 7, line 48), with the weight of the ingredients utilized being scaled down as shown in Table H.

Table H

INGREDIENTS	VASTA WEIGHTS (g)	SCALED DOWN WEIGHTS UTILIZED BY APPLICANTS (g)
Xylene	1006.15	57.50
Styrene monomer	321.11	18.35

INGREDIENTS	VASTA WEIGHTS (g)	SCALED DOWN WEIGHTS UTILIZED BY APPLICANTS (g)
Methyl methacrylate monomer	610.11	34.88
Hydroxyethyl acrylate monomer	107.04	6.12
Glycidyl methacrylate monomer	460.26	26.31
Tertiary butyl peracetate	62.44	3.56
Tertiary butyl peracetate	8.92	0.5101
Dehydrated castor fatty acid (C <sub>9-11</sub> drying oil fatty acids)	642.22	36.69
Tetrabutylammonium hydroxide	3.46	0.1981
Propylene glycol monomethyl ether acetate	278.30	15.90

Upon addition of portion 3 to the reaction mixture (see column 7, lines 31-37), the fatty acid phase separated from the rest of the polymer solution. The appearance of black flakes in the reaction mixture was noted. It was determined that these flakes were actually the painted lines and numbers from the thermometer. The solution was allowed to cool, and portion 4 was added as described in Example 1 of the Vasta patent. However, at this point, there was also phase separation of portion 4 from the other two solutions. As the reaction cooled, the polymer solution increased substantially in viscosity and became sufficiently thick that it could not be stirred, either magnetically or mechanically. Due to this inability to stir, and due to the phase separations, the reaction mixture

could not be formulated into a coating composition, and thus the composition cannot be formed into a film at all, let alone a film having the recited properties.

U.S. PATENT NO. 4,981,891 TO FELTER ET AL.

Example 1 of the Felter et al. patent was duplicated except that the quantity of ingredients were scaled down while maintaining the relative weight percentages of the ingredients. Additionally, two of the ingredients used in solution A of Example 1 (see the table in column 7, line 64 et seq.) could not be located. Specifically, Varstat® 66 is no longer produced so it was replaced with Adogen® 66. Adogen® 66 was determined to be the closest available chemical. The MSDS for Adogen® 66 is attached as Exhibit A.

Also, the choline methosulfate is no longer available. Attempts to synthesize the choline methosulfate failed, and literature describing procedures for preparing choline methosulfate could not be located. As a result, it was concluded that, due to the fact that the choline methosulfate was only a minor constituent in the isopropanol solution, this ingredient could be omitted without impacting the overall composition. Table I shows the scaled-down quantity of ingredients that were utilized in these tests.

Table I

INGREDIENTS	SCALED DOWN WEIGHTS UTILIZED BY APPLICANTS (g)
Adogen® 66 <sup>a</sup>	1.99
Choline methosulfate	0

INGREDIENTS	SCALED DOWN WEIGHTS UTILIZED BY APPLICANTS (g)
Isopropanol	28.01
Larostat® 264A	2.02

<sup>a</sup> was used in place of Varstat® 66

Table J below shows the weights of ingredients used to prepare the polymer binder solution.

Table J

INGREDIENTS	SCALED DOWN WEIGHTS UTILIZED BY APPLICANTS (g)
PMMA	26.04
Toluene	36.01
Methyl ethyl ketone	59.99
Methyl isobutyl ketone	16
Propylene glycol methyl ether acetate	10.0
Nuosperse® 657	0.0204

Utilizing the isopropanol solution and the polymer binder solution prepared as discussed above, the remaining steps of preparing the coating composition were carried out as described in that example.

The coating solution was spin-coated onto 4" silicon wafers, but the thickness measurements of the coating were unsuccessful. That is, the ellipsometer did not provide any thickness measurements at all, and an alpha stepper could not determine the thickness in a reproducible

Serial No.

Docket No. 27269-CON2

manner. Thus, it was concluded that there was not actually a coating on the wafer, but rather simply a precipitation of solids onto the wafer (this was confirmed by observing the grainy appearance on the wafer surface after coating). As a result the pre-bake thermal stability test or film shrinkage testing could not be carried out on the sample because a film could not be formed on the substrate.

I further declare that all statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that wilful, false statements and the like are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code, and such wilful false statements may jeopardize the validity of any patents issued from the patent application.

  
Xie Shao

Date:

8/10/2001